

FORM PTO-1390 (Modified)
(REV 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

A-398

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/830598

INTERNATIONAL APPLICATION NO.

PCT/JP00/06038

INTERNATIONAL FILING DATE

6 September 2000

PRIORITY DATE CLAIMED

9 September 1999

TITLE OF INVENTION

HALFTONE PHASE SHIFT PHOTOMASK, AND HALFTONE PHASE
SHIFT PHOTOMASK BLANK FOR THE FABRICATION OF THE SAME

APPLICANT(S) FOR DO/EO/US

Junji FUJIKAWA et al

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☒ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

Inventor Information Sheet (Patent Bibliographical Data)

Copy of Form PCT/IB/308

Form PTO-1449 and copies of documents cited thereon with 2nd copy of International Preliminary Examination Report
Letter

Express Mail #EL 719795338US

S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/830598

INTERNATIONAL APPLICATION NO.

PCT/JP00/06038

ATTORNEY'S DOCKET NUMBER

A-398

24. The following fees are submitted.:

CALCULATIONS PTO USE ONLY

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

- ☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1000.00
- ☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00
- ☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00
- ☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00
- ☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

\$860.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).

\$0.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	42 - 20 =	22	x \$18.00
Independent claims	2 - 3 =	0	x \$80.00

\$396.00

\$0.00

Multiple Dependent Claims (check if applicable).

☒

\$270.00

TOTAL OF ABOVE CALCULATIONS =

\$1,526.00

☐ Applicant claims small entity status. (See 37 CFR 1.27). The fees indicated above are reduced by 1/2.

\$0.00

SUBTOTAL =

\$1,526.00

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).

\$0.00

TOTAL NATIONAL FEE =

\$1,526.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).

☒

\$40.00

TOTAL FEES ENCLOSED =

\$1,566.00

Amount to be:

refunded

\$

charged

\$

- a. ☒ A check in the amount of \$1,566.00 to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☐ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. _____. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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SIGNATURE

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REGISTRATION NUMBER

April 27, 2001

DATE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

Junji FUJIKAWA et al

Art Unit:

S. N.

Examiner:

International S.N.: PCT/JP00/06038

Filed:

International Filing Date: 6 September 2000

For: HALFTONE PHASE SHIFT PHOTOMASK,
AND HALFTONE PHASE SHIFT PHOTOMASK
BLANK FOR THE FABRICATION OF THE SAME

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Please make the following amendments to this application
prior to examination thereof:

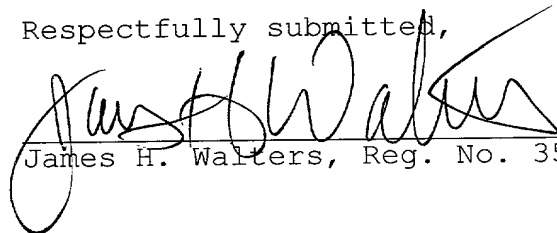
In the Drawings:

Please amend FIGS. 1-3, 7 and 8 as indicated in red on the
drawing sheets attached herewith.

REMARKS

The above amendments are submitted to place the application
into a format consistent with U.S. practice.

Respectfully submitted,


James H. Walters, Reg. No. 35,731

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~~FIG. 1~~

FIG. 1 (a)

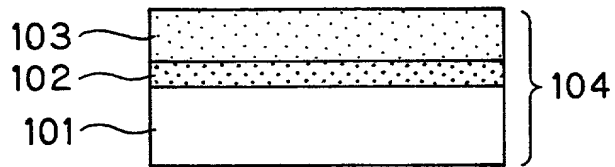


FIG. 1 (b)

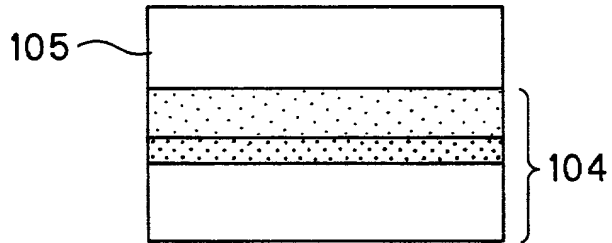


FIG. 1 (c)

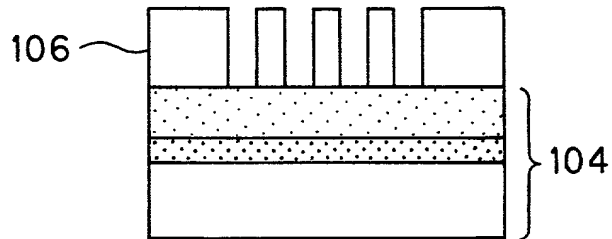
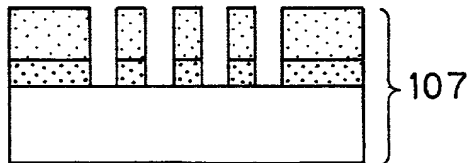


FIG. 1 (d)



~~FIG. 2~~

FIG. 2 (a)

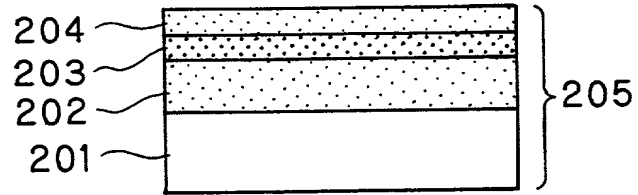
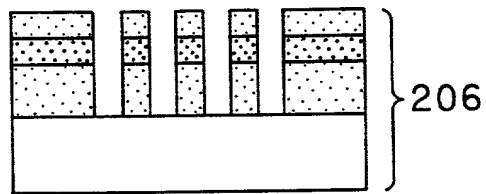


FIG. 2 (b)



~~FIG. 3~~

FIG. 3 (a)

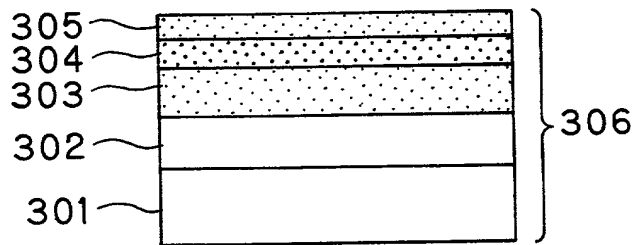
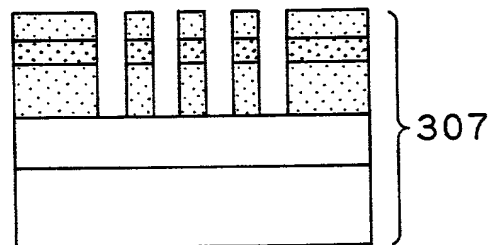


FIG. 3 (b)



~~FIG. 7~~

FIG. 7 (a)

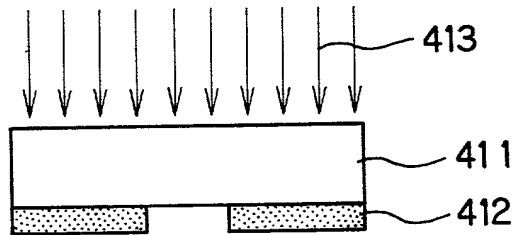


FIG. 7 (b)

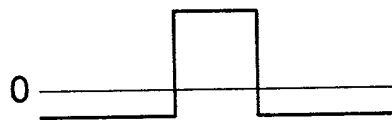


FIG 7 (c)

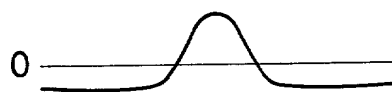
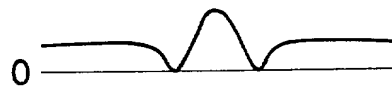


FIG. 7 (d)



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~~FIG. 8~~

FIG. 8 (a)

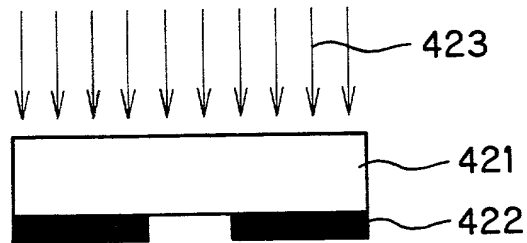


FIG. 8 (b)

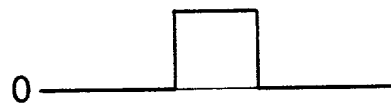


FIG. 8 (c)

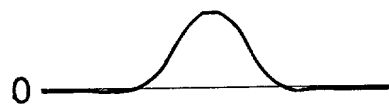
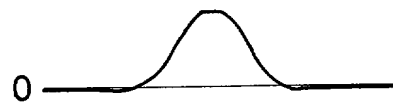


FIG. 8 (d)



SPECIFICATION

HALFTONE PHASE SHIFT PHOTOMASK, AND HALFTONE PHASE SHIFT
PHOTOMASK BLANK FOR THE FABRICATION OF THE SAME

ART FIELD

5 The present invention relates generally to a photomask
used for the fabrication of high-density integrated circuits
such as LSIs and a photomask blank for the fabrication of the
same, and more particularly to a halftone phase shift
photomask that enables projected images of minute size to be
10 obtained and a halftone phase shift photomask blank for the
fabrication of this halftone phase shift photomask.

BACKGROUND ART

Semiconductor integrated circuits such as LSIs are
fabricated by the repetition of a so-called lithography
15 process using a photomask. Possible applications of such
phase shift masks as set forth in JP-A 58-173744, JP-B 62-
59296, etc. to the formation of microcircuits in particular
have already been under investigation. Among others, the so-
called halftone phase shift photomask such as one set forth
20 in United States Patent No. 4,890,309, etc. has attracted
attention in view of expedited practical applications. For
instance, as disclosed in JP-A's 05-2259 and 05-127361, some
proposals have been made in respect of arrangements and
materials improved in yields and reduced in costs for the
25 purpose of practical applications.

Here a typical halftone phase shift photomask is briefly
explained with reference to Figs. 7 and 8. Figs. 7(a)
through 7(d) are illustrative of the principles of halftone

phase shift lithography, and Figs. 8(a) through 8(d) are illustrative of a conventional process. Figs. 7(a) and 8(a) are each a sectional view of a photomask, Figs. 7(b) and 8(b) are each illustrative of the amplitude of light on the photomask, Figs. 7(c) and 8(c) are each illustrative of the amplitude of light on a wafer, and Figs. 7(d) and 8(d) are each illustrative of the intensity of light on the wafer. Reference numerals 411 and 421 are each a transparent substrate, 422 a 100% light-blocking film, 412 a halftone phase shift film, and 413 and 423 are each incident light. By the term "halftone phase shift film" used herein is intended a film, in a single layer or multilayer form, having functions of substantially inverting the phase of transmitting exposure light with respect to the phase of exposure light passing through the air having the same optical length and attenuating the intensity of the light. According to the conventional process, the 100% light-blocking film 422 formed of chromium or the like is provided on the substrate 421 formed of quartz glass or the like, as shown in Fig. 8(a), thereby achieving a simple arrangement where a light transmitting portion of any desired pattern is formed. The light on the wafer has such a fan-shaped intensity distribution as shown in Fig. 8(d), resulting in poor resolution. With the halftone phase shift lithography, on the other hand, it is possible to achieve improvements in resolution, because the phase of light transmitting through the halftone phase shift mask 412 is substantially inverted with respect to the phase of light transmitting through its

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opening, so that the intensity of light at pattern boundaries on the wafer is reduced to zero as shown in Fig. 7(d) and, hence, such a fan-shaped intensity distribution is prevented.

Referring to the halftone phase shift photomask in general, the optimum phase difference is 180° , and the optimum transmittance is in the range of 1 to 20% (100% for the opening) as determined depending on the pattern to be transferred, transfer conditions, etc. A halftone phase shift mask must be fabricated in such a way as to meet its optimum phase difference and transmittance. Any deviation from the optimum values leads to changes in the correct exposure, etc., ending up with dimensional accuracy drops, a limited tolerance to focus, etc. Thus, the refractive index, extinction coefficient, thickness accuracy and thickness stability of the single layer or multilayer forming the halftone phase shift film are of vital importance.

To ensure the effect of the halftone phase shift photomask, the phase difference and transmittance thereof at an exposure wavelength are of vital importance. To reduce the influences of multiple scattering, etc. between the photomask and lenses in the photolithography process, the reflectance of the mask at an exposure wavelength should preferably be kept low as is the case with conventional photomasks, and most preferably be 20% or less. Regarding the appearance quality, dimensional accuracy, position accuracy, etc. of the pattern formed on the photomask, too, the photomask is required to have similar various properties to those needed for conventional photomasks. To ensure these

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properties, the optical properties of the photomask, for instance, its transmittance and reflectance at wavelengths at which various inspection and measuring devices are used in the masking process are also of vital importance. To be more specific, the photomask should have a transmittance and reflectance of 50% or less at wavelengths of 488 nm or less.

In this connection, halftone phase shift photomasks may be fabricated by means of PVD or CVD processes. In most cases, however, they are fabricated by a reactive sputtering process wherein main materials are used in the form of targets. The refractive index, extinction coefficient, thickness accuracy and stability of the film are basically determined by the film-formation process. For etching the phase difference shift film at the step of patterning the phase shift photomask, dry etching such as reactive ion etching is chiefly used. In the process of fabricating phase shift photomasks, washing is repeatedly carried out so as to improve their degree of cleanliness.

For instance, halftone phase shift films comprising any one of tantalum, an oxide of tantalum, a nitride of tantalum and a combined oxide and nitride of tantalum have been proposed as set forth in JP-A's 05-257264, 07-134396 and 07-281414.

In recent years, as the pattern to be formed becomes fine, it is required to make short the wavelength of exposure light used for lithography, and KrF excimer lasers of 248 nm wavelength are now put to practical use for patterns finer than the so-called 0.25 μm design rule. With expected

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further size reductions in view, ArF excimer lasers of 193 nm wavelength are under investigation. For halftone phase shift films used for halftone phase shift photomasks, too, the development of materials capable of achieving the optimum
5 phase difference and transmittance for these wavelengths and having stable refractive indices and extinction coefficients are in great demand.

However, conventional halftone phase shift films comprising any one of tantalum, an oxide of tantalum, a
10 nitride of tantalum and a combined oxide and nitride of tantalum, too, have several problems. For instance, a problem with films comprising tantalum or the oxide of tantalum is that when they have a thickness enough to have a phase difference of 180° at 248 nm wavelength, their
15 transmittance decreases to 1% or less that deviates the range of 1 to 20% thought of as being the optimum transmittance range.

For instance, the thickness vs. 248 nm wavelength phase difference and transmittance relations of a tantalum nitride
20 film formed on a synthetic quartz substrate by a reactive sputtering process using a pure tantalum target in a nitrogen atmosphere are shown in Fig. 9. As can be seen from Fig. 9, the phase difference increases in proportion to an increasing thickness and, at the same time, the transmittance becomes
25 low.

The tantalum nitride film has a phase difference of 180° at a thickness of 113 nm, but fails to have the transmittance

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needed for a phase shift photomask, because its transmittance is 0.06% at that thickness.

Films comprising the oxide of tantalum or the combined oxide and nitride of tantalum may have a phase difference of 180° and a transmittance of 1 to 20% as desired, both at 248 nm wavelength. However, these films cannot be inspected with precision by an inspection device for ensuring the appearance quality of a mask or a measuring device because their transmittance exceeds 50% at an inspection wavelength.

For instance, the thickness vs. phase difference and transmittance relations of a tantalum oxide film formed on a synthetic quartz substrate by a reactive sputtering process using a pure tantalum target in a nitrogen atmosphere are shown in Fig. 10. As shown in Fig. 10, the tantalum oxide film may be used as a phase shift mask because its phase difference and transmittance are 180° and 13%, respectively, at 81 nm thickness and 248 nm wavelength. A spectral transmittance curve and a spectral reflectance curve for an 81 nm thick tantalum oxide film are shown in Figs. 11 and 12, respectively. As can be seen from Fig. 11, a transmittance of 80% or greater is obtained at wavelengths of 300 nm or greater. As can be seen from Fig. 12, a reflectance of 29% is obtained at 248 nm wavelength; it is impossible to obtain any sufficiently low reflectance at the exposure wavelength.

On the other hand, various inspection and measuring devices are used in the masking process for the purpose of ensuring various property requirements for a photomask, for instance, its appearance quality, dimensional accuracy and

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position accuracy. These devices are now mainly used with light of 365 nm to 633 nm wavelengths to make an inspection and measurement through a contrast of light intensity between a light transmitting portion and a light blocking portion.

- 5 For precise measurement, the light blocking portion, viz., the halftone phase shift film must have a low transmittance or a transmittance of at least 50% or less in the wavelength range of 365 nm to 488 nm.

- From the foregoing, it is found that it is very
10 difficult to inspect and measure the tantalum oxide film with precision to check whether or not it is acceptable as a halftone phase shift photomask, and so it is impossible to ensure the quality needed for a photomask.

- When a tantalum oxide film is formed at such a thickness
15 as to ensure a phase difference of 180° at 248 nm wavelength by using a specific tantalum to oxygen ratio or adding nitrogen thereto to obtain a composite oxide and nitride film, its transmittance may be controlled to some extent. However, when this film is provided in a single layer film,
20 it is impossible to obtain a transmittance of 1% or greater at 248 nm wavelength and a transmittance of 50% or less at wavelengths of 365 nm to 488 nm.

- When phase shift photomasks comprising the oxide of tantalum, the nitride of tantalum and the combined oxide and
25 nitride of tantalum are patterned by dry etching, it is difficult to gain precise phase difference control because a transparent substrate such as a quartz substrate is etched simultaneously with the tantalum film by a fluorine-base gas

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used at the dry etching step, giving rise to a phase difference.

SUMMARY OF THE INVENTION

In view of such states of the prior art as mentioned
5 above, an object of the present invention is to provide a
halftone phase shift photomask which is controlled with
precision in terms of its transmittance at a wavelength
applied to inspection, and measuring equipment, so that its
quality can easily be assured even when its phase difference
10 at an exposure wavelength is controlled at 180° with
precision and its transmittance is set at 1 to 20% as desired
at that wavelength as well as a halftone phase shift
photomask blank for the fabrication of the same.

According to the present invention, the aforesaid object
15 is achievable by the provision of a halftone phase shift
photomask comprising on a transparent substrate and a
halftone phase shift film containing at least tantalum,
oxygen, carbon and nitrogen, characterized in that the
halftone phase shift photomask has a multilayer structure
20 comprising at least two or more different layers.

Each layer is formed of a film wherein the composition
ratio of tantalum atoms and oxygen atoms is such that at
least 100 oxygen atoms are contained per 100 tantalum atoms,
a film wherein the composition ratio of tantalum atoms and
25 other atoms is such that 100 or less other atoms are
contained per 100 tantalum atoms or a film wherein the
composition ratio of tantalum atoms and oxygen and nitrogen
atoms is such that 50 to 250 oxygen atoms and 1 to 200

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nitrogen atoms are contained per 100 tantalum atoms. Two or more such films are laminated one upon another while the thickness of each film is controlled, so that the photomask can have a phase difference of 180° and a transmittance of 1 to 13% as desired, both at 248 nm wavelength and a transmittance of 50% or less at a wavelength of 488 nm or less.

Preferably in this case, the multilayer film comprising two or more difference film should include at least one layer in which 100 or less other atoms are contained per 100 tantalum atoms.

The halftone phase shift photomask of the invention has a structure wherein a film with the composition ratio of tantalum atoms and oxygen atoms being such that at least 100 oxygen atoms are contained per 100 tantalum atoms is laminated on a film with the composition ratio of tantalum atoms and other atoms being such that 100 or less other atoms are contained per 100 tantalum atoms, or a structure wherein a film with the composition ratio of tantalum atoms and oxygen and nitrogen atoms being such that 50 to 250 oxygen atoms and 1 to 200 nitrogen atoms are contained per 100 tantalum atoms is laminated on a film with the composition ratio of tantalum atoms and other atoms being such that 100 or less other atoms are contained per 100 tantalum atoms. Thus, the halftone phase shift photomask can have a phase difference of 180° and a transmittance of 1 to 20% as desired, both at 248 nm wavelength, a transmittance of 50% or

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less at a wavelength of 488 nm or less and a reflectance of 20% or less at 248 nm wavelength.

5 The halftone phase shift photomask of the invention has a structure wherein a film with the composition ratio of tantalum atoms and other atoms being such that 100 or less other atoms are contained per 100 tantalum atoms is directly laminated on the transparent substrate, with subsequent films laminated successively thereon. The film with the composition ratio of tantalum atoms and other atoms being
10 such that 100 or less other atoms are contained per 100 tantalum atoms can be etched with a chlorinous gas whereas the transparent substrate such as a synthetic quartz substrate is unsusceptible to etching with a chlorine-base etching gas. Accordingly, when the phase shift film is dry
15 etched, the film formed on the transparent substrate such as a synthetic quartz substrate, with the composition ratio of tantalum atoms and other atoms being such that 100 or less other atoms are contained per 100 tantalum atoms, can be etched using a chlorine-base gas. Thus, the phase shift film
20 can be patterned while the transparent substrate such as a synthetic quartz substrate remains unetched, so that no phase difference occurs at that portion, resulting in precise phase difference control.

25 The halftone phase shift photomask of the invention has a structure wherein an etching stopper layer is formed on the transparent substrate, with halftone phase shift films laminated successively thereon. Accordingly, even when the phase shift film is patterned by dry etching using a chlorine

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or fluorine-base gas, the transparent substrate such as a synthetic quartz substrate remains unetched, so that no phase difference occurs at that portion, resulting in precise phase difference control.

5 Preferably in this case, the etching stopper layer should be formed of a material such as hafnium oxide, which has sufficient etching resistance and whose transmittance at 248 nm wavelength does not drop even when provided on the transparent substrate with a thickness enough to function as
10 a stopper, for instance, with a thickness of about 50 nm.

It is here understood that the present invention also encompasses a halftone phase shift photomask blank for the fabrication of the aforesaid halftone phase shift photomask.

15 The advantages of the present invention are now explained. The present invention provides a halftone phase shift photomask and halftone phase shift photomask blank comprising on a transparent substrate a halftone phase shift film containing at least tantalum, oxygen, carbon and nitrogen, characterized by having a multilayer structure
20 comprising two or more different films. By thickness control of each film, the halftone phase shift photomask is allowed to have a phase difference of 180° and a transmittance of 1 to 20% as desired, both at 248 nm wavelength, so that improved resolution can be obtained at a lithography step.
25 Having a transmittance of 50% or less at a wavelength of 488 nm or less, this halftone phase shift photomask can also be inspected with precision by means of inspection, and measuring equipment for insuring its appearance quality.

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FDZ240.8650E860

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The halftone phase shift photomask, or the blank therefor, of the invention has a structure wherein a film with the composition ratio of tantalum atoms and oxygen atoms being such that at least 100 oxygen atoms are contained per 100 tantalum atoms is laminated on a film with the composition ratio of tantalum atoms and other atoms being such that 100 or less other atoms are contained per 100 tantalum atoms, or a structure wherein a film with the composition ratio of tantalum atoms and oxygen and nitrogen atoms being such that 50 to 250 oxygen atoms and 1 to 200 nitrogen atoms are contained per 100 tantalum atoms is laminated on a film with the composition ratio of tantalum atoms and other atoms being such that 100 or less other atoms are contained per 100 tantalum atoms. Thus, the halftone phase shift photomask can have a phase difference of 180° and a transmittance of 1 to 20% as desired, both at 248 nm wavelength, a transmittance of 50% or less at a wavelength of 488 nm or less and a reflectance of 20% or less at 248 nm wavelength. For this reason, multiple scattering, etc. can be prevented from occurring between the phase shift photomask and stepper lenses at an exposure wavelength in the lithography step, so that more improved resolution can be obtained.

The halftone phase shift photomask, or the blank therefor, of the present invention has a structure wherein a film with the composition ratio of tantalum atoms and other atoms being such that 100 or less other atoms are contained per 100 tantalum atoms is directly laminated on the

transparent substrate, with subsequent films laminated successively thereon, or a structure wherein an etching stopper layer is formed on the transparent substrate, with halftone phase shift films laminated successively thereon.

5 This enables only the halftone film to be selectively etched, so that there is no phase difference error which may otherwise result from etching of the transparent substrate such as a synthetic quartz substrate. It is thus possible to provide a phase shift photomask controlled with high
10 precision in terms of phase difference.

BRIEF EXPLANATION OF THE DRAWINGS

Figs. 1(a) through 1(d) are illustrative of steps of fabricating a halftone phase shift mask blank according to Example 1 of the invention, and steps of processing the blank
15 to obtain a halftone phase shift photomask.

Figs. 2(a) and 2(b) are illustrative of steps of fabricating a halftone phase shift photomask according to Example 2 of the invention.

Figs. 3(a) and 3(b) are illustrative of steps of fabricating a halftone phase shift mask blank according to
20 Example 3 of the invention.

Fig. 4 is a spectral transmittance curve for the halftone phase shift photomask of Example 1.

Fig. 5 is a spectral transmittance curve for the
25 halftone phase shift photomask of Example 2.

Fig. 6 is a spectral transmittance curve for the halftone phase shift photomask of Example 3.

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Figs. 7(a) through 7(d) are illustrative of the principles of halftone phase shift lithography.

Figs. 8(a) through 8(d) are illustrative of conventional lithography as compared with Figs. 7(a) through 7(d).

5 Fig. 9 is a graph illustrative of the thickness vs. phase difference/transmittance relations for a tantalum nitride film.

10 Fig. 10 is a graph illustrative of the thickness vs. phase difference/transmittance relations for a tantalum oxide film.

Fig. 11 is a spectral transmittance curve for an 81 nm thick tantalum oxide film.

Fig. 12 is a spectral reflectance curve for an 81 nm thick tantalum oxide film.

15 BEST MODE FOR CARRYING OUT THE INVENTION

The halftone phase shift photomask and halftone phase shift photomask blank according to the present invention are now explained specifically with reference to their examples.
Example 1

20 Example 1 of the halftone phase shift photomask blank and halftone phase shift photomask according to the present invention are explained with reference to Figs. 1(a) through 1(d). As shown in Fig. 1(a), the following two layers were successively formed on an optically polished, well-washed
25 synthetic quartz substrate 101 by sputtering under the following conditions, the first layer comprising a film 102 composed mainly of tantalum and the second layer comprising a film 103 composed mainly of tantalum and oxygen. In this

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way, a halftone phase shift photomask blank 104 of a double-layer structure was obtained.

Conditions for the first layer:

Sputtering system: DC magnetron sputtering system
5 Target: Metallic tantalum
Gas and flow rate: Argon gas 60 sccm
Sputtering pressure: 15.0 millitorr
Sputtering power: 0.8 kilowatts

Conditions for the second layer:

10 Sputtering system: DC magnetron sputtering system
Target: Metallic tantalum
Gases and flow rates: Argon gas 60 sccm plus carbonic
acid gas 40 sccm
Sputtering pressure: 5.0 millitorr
15 Sputtering power: 1 kilowatt
Here the formed first layer had a thickness of 15 nm and
the second layer had a thickness of 62 nm.

By measurement on a commercially available transmittance
meter (MCPD2000, Otsuka Denshi Ltd.), the phase shift film
20 obtained under the aforesaid conditions was found to have a
transmittance of 6.02% at 248 nm wavelength and a
transmittance of 50% or less at a wavelength of 488 nm or
less. A spectral transmittance curve for this phase shift
film is shown in Fig. 4.

25 By X-ray photoelectron spectroscopy of the phase shift
film obtained under the aforesaid conditions, the first layer
was found to contain 16 oxygen atoms per 100 tantalum atoms
and the second layer was found to contain 150 oxygen atoms

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per 100 tantalum atoms. For this X-ray photoelectron spectroscopy, ESCALAB210 (VG SCIENTIFIC) was used to analyze each layer after Ar ion beam etching.

Next, the step of patterning and processing this
5 halftone phase shift photomask blank 104 into a photomask is now explained. As shown in Fig. 1(b), a commercially available electron beam resist (ZEP7000, Nippon Zeon Co., Ltd.) is coated on the halftone phase shift photomask blank 104 at a post-baking thickness of 300 nm, and subsequently
10 baked at 110°C for 20 minutes to obtain an electron beam resist film 105.

Then, a photomask electron beam lithography system is used to obtain a latent image in the desired pattern. Finally, this latent image is developed with a dedicated
15 developing solution ZED500 to obtain such a desired resist pattern 106 as shown in Fig. 1(c). Using this resist pattern 106 as a mask, inductive coupled plasma etching is carried out under the following conditions for the dry etching of halftone phase shift film.

20 Etching system: Inductive coupled plasma etcher
Gases and flow rates: Sulfur hexafluoride gas 18 sccm
plus oxygen gas 4 sccm

Etching pressure: 10 millitorr

Etching power: 250 watts

25 Bias power: 10 watts

After completion of etching, the halftone phase shift film is surface treated with ozone while irradiated with ultraviolet radiation to remove an unnecessary portion of the

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resist, thereby obtaining such a halftone phase shift photomask 107 as shown in Fig. 1(d). By measurement using a commercially available phase difference meter for phase shift masks (MPM248, Laser Tech Co., Ltd.), this halftone phase shift photomask was found to have a phase difference of 179.8° at 248 nm wavelength.

In the thus obtained phase shift photomask, the phase difference at 248 nm wavelength was controlled with precision in the vicinity of 180° and the transmittance at 488 nm wavelength was 50% or less, so that this photomask could be inspected with the highest sensitivity using an appearance inspection device and a measuring device. This example was carried out for the purpose of obtaining a halftone phase shift photomask having a most general transmittance of 6% at 248 nm wavelength. It is understood, however, that any phase shift photomask having a phase difference of 180° at the desired transmittance can easily be obtained by changing the thickness of the first and second layers.

In this example, etching was carried out using an inductive coupled plasma etcher in the process of forming the phase shift photomask blank into the photomask. If the upper or second layer 103 is first etched under the same conditions as mentioned above and the lower or first layer 102 composed mainly of tantalum is then etched using a chlorine-base gas, it is then possible to gain phase difference control with even higher precision because the transparent substrate 101 such as a synthetic quartz substrate remains unetched. Set out below are specific etching conditions.

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Etching system: Inductive coupled plasma etcher

Gas and flow rate: Chlorine gas 21 sccm

Etching pressure: 5 millitorr

Etching power: 250 watts

5 Bias power: 25 watts

Example 2

Example 2 of the halftone phase shift photomask blank and halftone phase shift photomask according to the present invention are explained with reference to Figs. 2(a) and
10 2(b). As shown in Fig. 2(a), the following three layers were successively formed on an optically polished, well-washed synthetic quartz substrate 201 by sputtering under the following conditions, the first layer comprising a film 202 composed mainly of tantalum and oxygen, the second layer
15 comprising a film 203 composed mainly of tantalum, and the third layer comprising a film 204 composed mainly of tantalum and oxygen. In this way, a halftone phase shift photomask blank 205 of a triple-layer structure was obtained.

Conditions for the first layer:

20 Sputtering system: DC magnetron sputtering system

Target: Metallic tantalum

Gases and flow rates: Argon gas 10 sccm plus carbonic
acid gas 40 sccm

Sputtering pressure: 5.0 millitorr

25 Sputtering power: 1.0 kilowatt

Conditions for the second layer:

Sputtering system: DC magnetron sputtering system

Target: Metallic tantalum

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Gas and flow rate: Argon gas 60 sccm

Sputtering pressure: 15.0 millitorr

Sputtering power: 0.8 kilowatts

Conditions for the third layer:

5 Sputtering system: DC magnetron sputtering system

Target: Metallic tantalum

Gases and flow rates: Argon gas 10 sccm plus carbonic
acid gas 40 sccm

Sputtering pressure: 5.0 millitorr

10 Sputtering power: 1.0 kilowatt

Here the formed first layer had a thickness of 50 nm,
the second layer had a thickness of 15 nm and the third layer
had a thickness of 12 nm.

By measurement on a commercially available transmittance
15 meter (MCPD2000, Otsuka Denshi Ltd.), the phase shift film
obtained under the aforesaid conditions was found to have a
transmittance of 6.00% at 248 nm wavelength and a
transmittance of 50% or less at a wavelength of 488 nm or
less. A spectral transmittance curve for this phase shift
20 film is shown in Fig. 5. By measurement on a commercially
available reflectance meter (Automatic Spectral Luminosity
Meter 330, Hitachi Ltd.), the phase shift film was found to
be a low reflectance film as can be seen from a surface
reflectance of 14.8% at 248 nm wavelength. A spectral
25 reflectance curve for this phase shift film is shown in Fig.
6.

The step of processing this halftone phase shift
photomask blank 205 into a halftone phase shift photomask 206

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shown in Fig. 2(b) is the same as in Example 1. By measurement using a commercially available phase difference meter for phase shift masks (MPM248, Laser Tech Co., Ltd.), this halftone phase shift photomask 206 was found to have a
5 phase difference of 180.1° at 248 nm wavelength.

In the thus obtained phase shift photomask, the phase difference at 248 nm wavelength was precisely controlled in the vicinity of 180° and the transmittance at 488 nm wavelength was 50% or less, so that this photomask could be
10 inspected with the highest sensitivity using an appearance inspection device and a measuring device, as in Example 1. This example was carried out for the purpose of obtaining a halftone phase shift photomask having a most general transmittance of 6% at 248 nm wavelength. It is understood,
15 however, that any phase shift photomask having a phase difference of 180° at the desired transmittance can easily be obtained by changing the thickness of the first and second layers, or the third layer, as in Example 1. It is also understood that the halftone phase shift photomask has a
20 reflectance of as low as 14.8% at 248 nm wavelength, so that even higher resolution can be obtained in the photolithography process.

Even when instead of the film composed mainly of tantalum and oxygen, a film composed mainly of tantalum,
25 oxygen and nitrogen is used for the third layer, similar advantages are obtainable. Set out are one exemplary film-formation conditions.

Conditions for the third layer:

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Sputtering system: DC magnetron sputtering system

Target: Metallic tantalum

Gases and flow rates: Argon gas 10 sccm plus carbonic
acid gas 40 sccm plus nitrogen
gas 30 sccm

Sputtering pressure: 5.0 millitorr

Sputtering power: 1.0 kilowatt

Here a metallic tantalum film was formed on a synthetic quartz substrate at a thickness of 150 nm, and a film comprising tantalum, oxygen and nitrogen was formed thereon at a thickness of 28 nm under the aforesaid conditions. X-ray photoelectron spectroscopy showed that 136 oxygen atoms and 17 nitrogen atoms are contained per 100 tantalum atoms. For this X-ray photoelectron spectroscopy, ESCALAB210 (VG SCIENTIFIC) was used to analyze each layer after Ar ion beam etching.

Example 3

Example 3 of the halftone phase shift photomask blank and halftone phase shift photomask according to the present invention are explained with reference to Figs. 3(a) and 3(b). As shown in Fig. 3(a), the following four layers were successively formed on an optically polished, well-washed synthetic quartz substrate 301 by sputtering under the following conditions, the first layer comprising an etching stopper layer 302 composed mainly of hafnium oxide, the second layer comprising a film 303 composed mainly of tantalum and oxygen, the third layer comprising a film 304 composed mainly of tantalum, and the fourth layer comprising

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a film 305 composed mainly of tantalum and oxygen. In this way, a halftone phase shift photomask blank 306 of a four-layer structure was obtained.

Conditions for the first layer:

- 5 Sputtering system: DC magnetron sputtering system
 Target: Metallic hafnium
 Gases and flow rates: Argon gas 10 sccm plus carbonic
 acid gas 40 sccm
 Sputtering pressure: 5.0 millitorr
10 Sputtering power: 1.0 kilowatt

Conditions for the second layer:

- Sputtering system: DC magnetron sputtering system
 Target: Metallic tantalum
 Gas and flow rate: Argon gas 10 sccm plus carbonic
15 acid gas 40 sccm
 Sputtering pressure: 5.0 millitorr
 Sputtering power: 1.0 kilowatt

Conditions for the third layer:

- Sputtering system: DC magnetron sputtering system
20 Target: Metallic tantalum
 Gas and flow rate: Argon gas 60 sccm
 Sputtering pressure: 15.0 millitorr
 Sputtering power: 0.8 kilowatts

Conditions for the fourth layer:

- 25 Sputtering system: DC magnetron sputtering system
 Target: Metallic tantalum
 Gas and flow rate: Argon gas 10 sccm plus carbonic
 acid gas 40 sccm

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Sputtering pressure: 5.0 millitorr

Sputtering power: 1.0 kilowatt

Here the formed first layer had a thickness of 50 nm, the second layer had a thickness of 50 nm, the third layer had a thickness of 15 nm, and the fourth layer had a thickness of 12 nm.

The phase shift film obtained under the aforesaid conditions had the same transmittance as in Example 2.

The step of processing this halftone phase shift photomask blank 306 into a halftone phase shift photomask 307 shown in Fig. 3(b) is the same as in Example 1. By measurement using a commercially available phase difference meter for phase shift masks (MPM248, Laser Tech Co., Ltd.), this halftone phase shift photomask 307 was found to have a phase difference of 180.1° at 248 nm wavelength.

In the thus obtained phase shift photomask, the phase difference at 248 nm wavelength was precisely controlled in the vicinity of 180° and the transmittance at 488 nm wavelength was 50% or less, so that this photomask could be inspected with the highest sensitivity using an appearance inspection device and a measuring device, as in Example 1. This example was carried out for the purpose of obtaining a halftone phase shift photomask having a most general transmittance of 6% at 248 nm wavelength. It is understood, however, that any phase shift photomask having a phase difference of 180° at the desired transmittance can easily be obtained by changing the thickness of the first and second layers, or the third layer, as in Example 1. It is also

understood that the halftone phase shift photomask has a reflectance of as low as 14.8% at 248 nm wavelength, so that even higher resolution can be obtained in the photolithography process.

5 In this example, etching was carried out using an inductive coupled plasma etching system in the process of processing the phase shift photomask blank into a photomask. However, if this etching is finished while the aforesaid conditions are maintained all the time, it is then possible
10 to gain more precise phase difference control, because the transparent substrate such as a quartz substrate remains unetched by virtue of the provision of the etching stopper layer thereon.

POSSIBILITY OF UTILIZATION IN INDUSTRY

15 With the halftone phase shift photomask or the halftone phase shift photomask blank according to the invention, it is possible to obtain a transmittance of 1 to 13% at 248 nm wavelength and a transmittance of 50% or less in the wavelength range of 365 nm to 633 nm, as can be understood
20 from the foregoing explanations, so that an inspection can easily be carried out so as to ensure the quality of photomasks. In addition, it is possible to achieve a reflectance of 20% or less at 248 nm wavelength and, hence, to obtain a halftone phase shift photomask of improved
25 practical value, which is less susceptible to the influences of multiple scattering, etc. in the photolithography process. By the direct provision of an etching stopper layer on the transparent substrate, it is possible to fabricate a halftone

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phase shift photomask which is free from any phase difference caused by the etching of the transparent substrate and so is improved in phase precision.

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WHAT WE CLAIM IS:

1. A halftone phase shift photomask comprising on a transparent substrate and a halftone phase shift film containing at least tantalum, oxygen, carbon and nitrogen, 5 which photomask has a multilayer structure comprising at least two or more different layers.

2. The halftone phase shift photomask according to claim 1, which includes at least one layer wherein the composition ratio of tantalum atoms and oxygen atoms is such 10 that at least 100 oxygen atoms are contained per 100 tantalum atoms.

3. The halftone phase shift photomask according to claim 1, which includes at least one layer wherein the composition ratio of tantalum atoms and other atoms is such 15 that 100 or less other atoms are contained per 100 tantalum atoms.

4. The halftone phase shift photomask according to claim 1, which includes at least one layer wherein the composition ratio of tantalum atoms and oxygen and nitrogen 20 atoms is such that 50 to 250 oxygen atoms and 1 to 200 nitrogen atoms are contained per 100 tantalum atoms.

5. The halftone phase shift photomask according to claim 1, which has a structure wherein a film with the composition ratio of tantalum atoms and oxygen atoms being 25 such that at least 100 oxygen atoms are contained per 100 tantalum atoms is laminated on a film with the composition ratio of tantalum atoms and other atoms being such that 100 or less other atoms are contained per 100 tantalum atoms.

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6. The halftone phase shift photomask according to claim 1, which has a structure wherein a film with the composition ratio of tantalum atoms and oxygen and nitrogen atoms being such that 50 to 250 oxygen atoms and 1 to 200 nitrogen atoms are contained per 100 tantalum atoms is laminated on a film with the composition ratio of tantalum atoms and other atoms being such that 100 or less other atoms are contained per 100 tantalum atoms.

7. The halftone phase shift photomask according to claim 1, which has a structure wherein a film with the composition ratio of tantalum atoms and other atoms being such that 100 or less other atoms are contained per 100 tantalum atoms is directly formed on the transparent substrate, with subsequent films laminated successively thereon.

8. The halftone phase shift photomask according to any one of claims 1 to 7, which has a structure wherein an etching stopper layer is formed on the transparent substrate, with halftone phase shift films laminated successively thereon.

9. The halftone phase shift photomask according to claim 8, which has a structure wherein halftone phase shift films are successively laminated on the etching stopper layer formed of a film composed mainly of hafnium oxide.

10. A halftone phase shift photomask blank comprising on a transparent substrate a halftone phase shift film containing at least tantalum, oxygen, carbon and nitrogen,

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which has a multilayer structure comprising two or more layers.

11. The halftone phase shift photomask blank according to claim 10, which includes at least one layer wherein the composition ratio of tantalum atoms and oxygen atoms is such that at least 100 oxygen atoms are contained per 100 tantalum atoms.

12. The halftone phase shift photomask blank according to claim 10, which includes at least one layer wherein the composition ratio of tantalum atoms and other atoms is such that 100 or less other atoms are contained per 100 tantalum atoms.

13. The halftone phase shift photomask blank according to claim 10, which includes at least one layer wherein the composition ratio of tantalum atoms and oxygen and nitrogen atoms is such that 50 to 250 oxygen atoms and 1 to 200 nitrogen atoms are contained per 100 tantalum atoms.

14. The halftone phase shift photomask blank according to claim 10, which has a structure wherein a film with the composition ratio of tantalum atoms and oxygen atoms being such that at least 100 oxygen atoms are contained per 100 tantalum atoms is laminated on a film with the composition ratio of tantalum atoms and other atoms being such that 100 or less other atoms are contained per 100 tantalum atoms.

15. The halftone phase shift photomask blank according to claim 10, which has a structure wherein a film with the composition ratio of tantalum atoms and oxygen and nitrogen atoms being such that 50 to 250 oxygen atoms and 1 to 200

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nitrogen atoms are contained per 100 tantalum atoms is laminated on a film with the composition ratio of tantalum atoms and other atoms being such that 100 or less other atoms are contained per 100 tantalum atoms.

5 16. The halftone phase shift photomask blank according to claim 10, which has a structure wherein a film with the composition ratio of tantalum atoms and other atoms being such that 100 or less other atoms are contained per 100 tantalum atoms is directly formed on the transparent
10 substrate, with subsequent films laminated successively thereon.

 17. The halftone phase shift photomask blank according to any one of claims 10 to 16, which has a structure wherein an etching stopper layer is formed on the transparent
15 substrate, with halftone phase shift films laminated successively thereon.

 18. The halftone phase shift photomask blank according to claim 17, which has a structure wherein halftone phase shift films are successively laminated on the etching stopper
20 layer formed of a film composed mainly of hafnium oxide.

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ABSTRACT OF THE DISCLOSURE

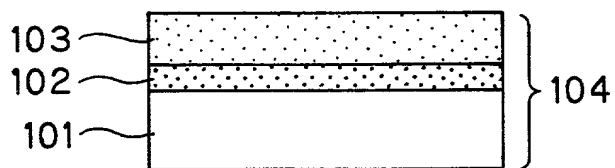
The invention relates to a halftone phase shift photomask which is controlled with precision in terms of its transmittance at a wavelength applied to inspection, and
5 measuring equipment, so that its quality can easily be assured even when its phase difference at an exposure wavelength is controlled at 180°C with precision and its transmittance is set at 1 to 20% as desired at that wavelength. The halftone phase shift photomask (107)
10 comprises on a transparent substrate (101) and a halftone phase shift film containing at least tantalum, oxygen, carbon and nitrogen, and has a multilayer structure comprising at least two or more different layers (102) and (103).

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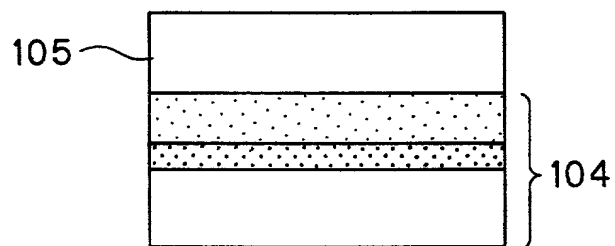
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FIG. 1

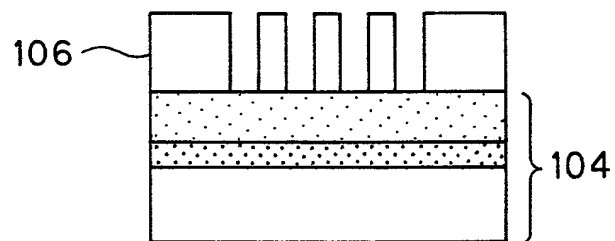
(a)



(b)



(c)



(d)

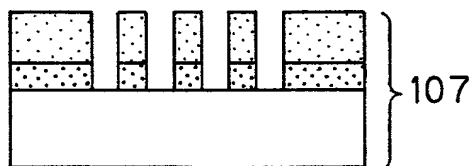
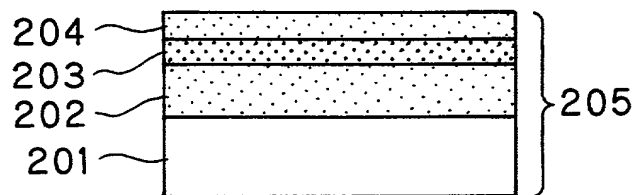


FIG. 2

(a)



(b)

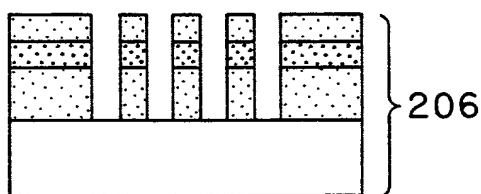
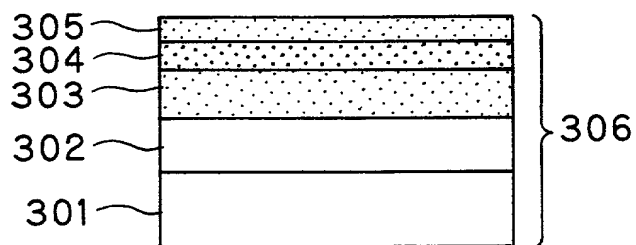


FIG. 3

(a)



(b)

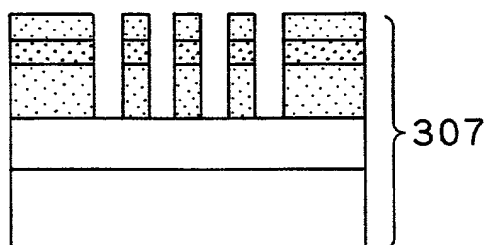


FIG. 4

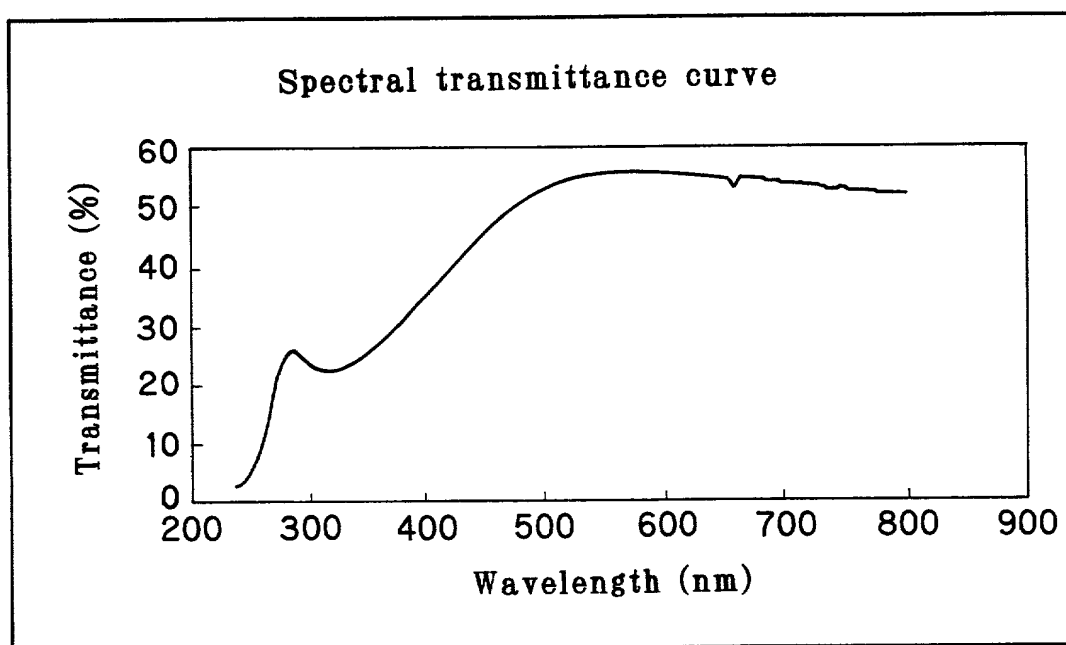


FIG. 5

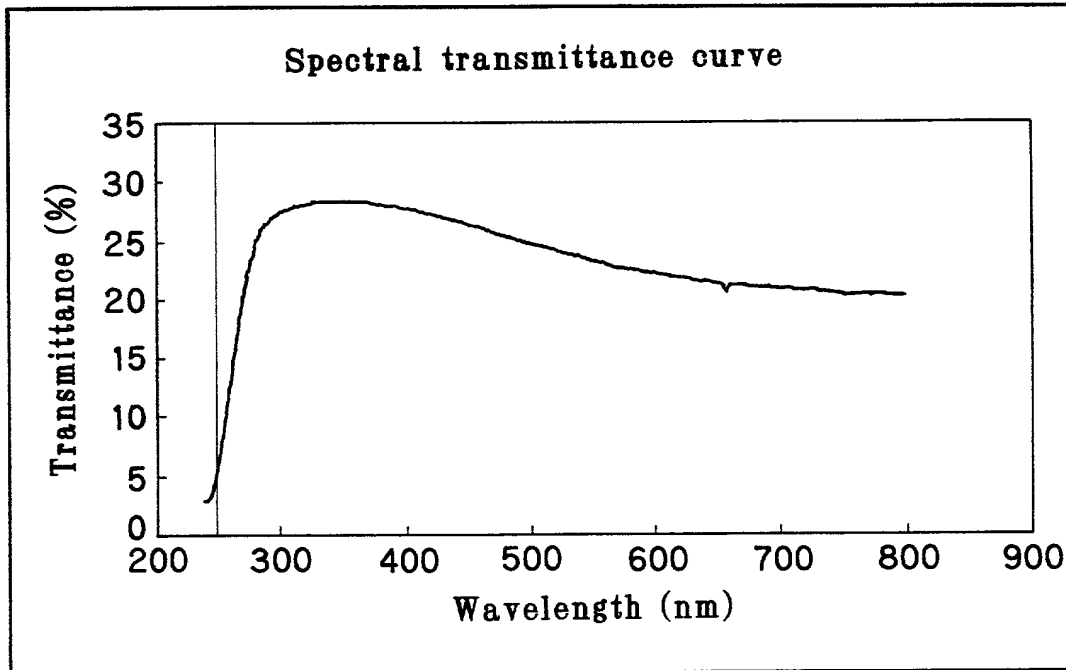


FIG. 6

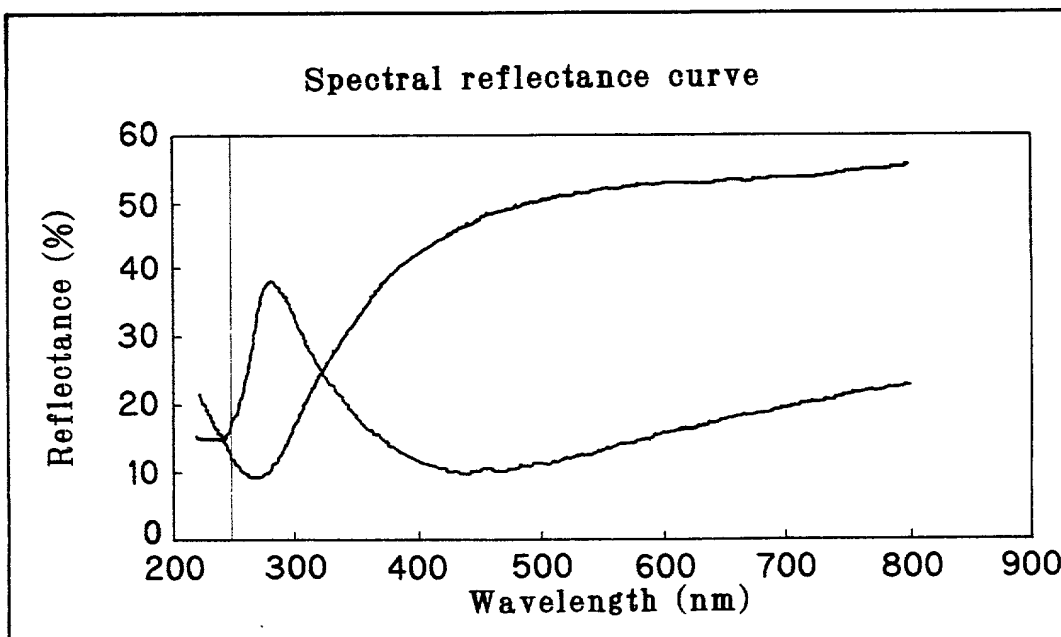
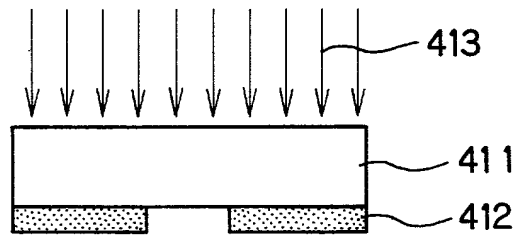
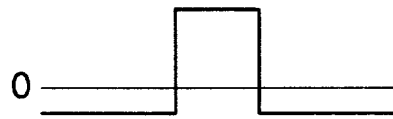


FIG. 7

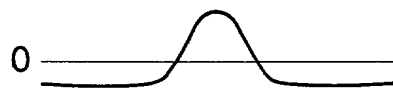
(a)



(b)



(c)



(d)

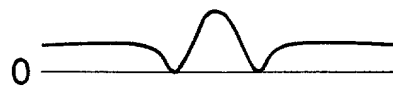


FIG. 8

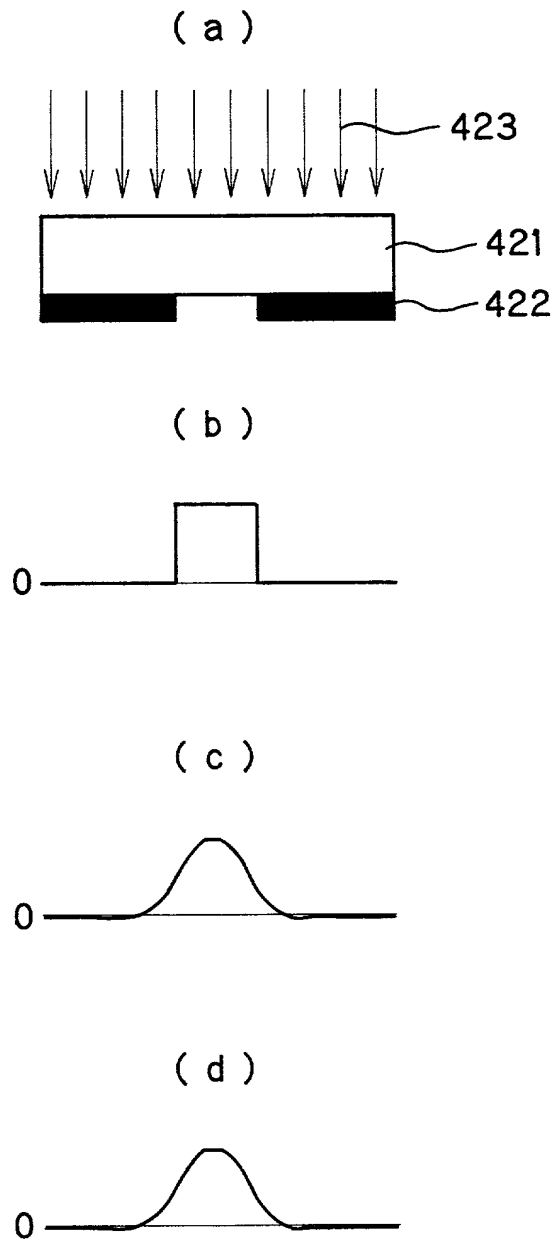


FIG. 9

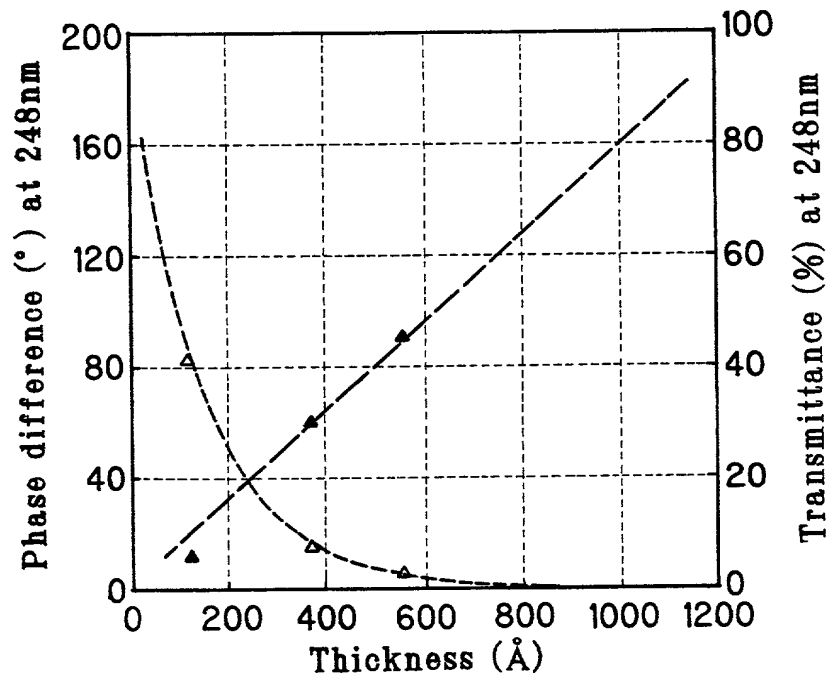


FIG. 10

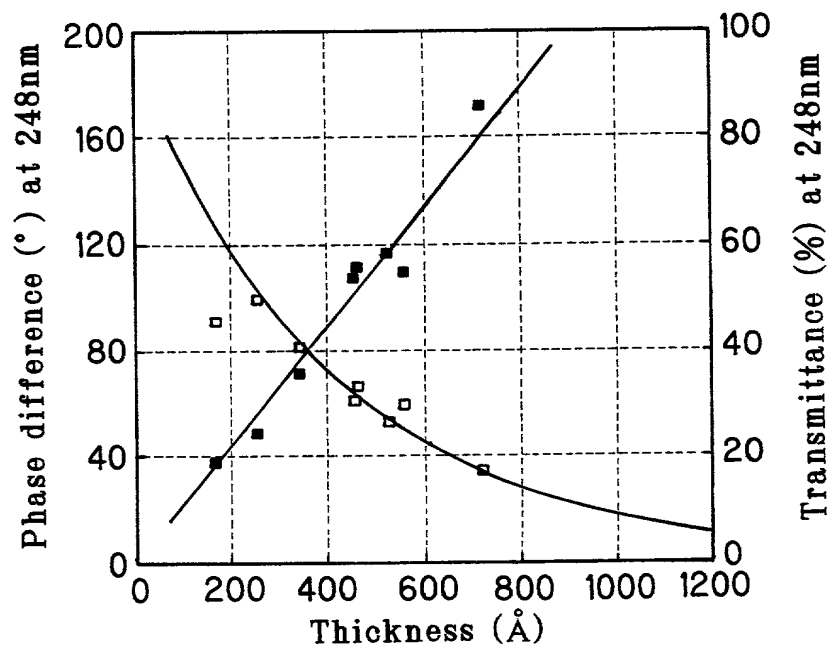


FIG. 11

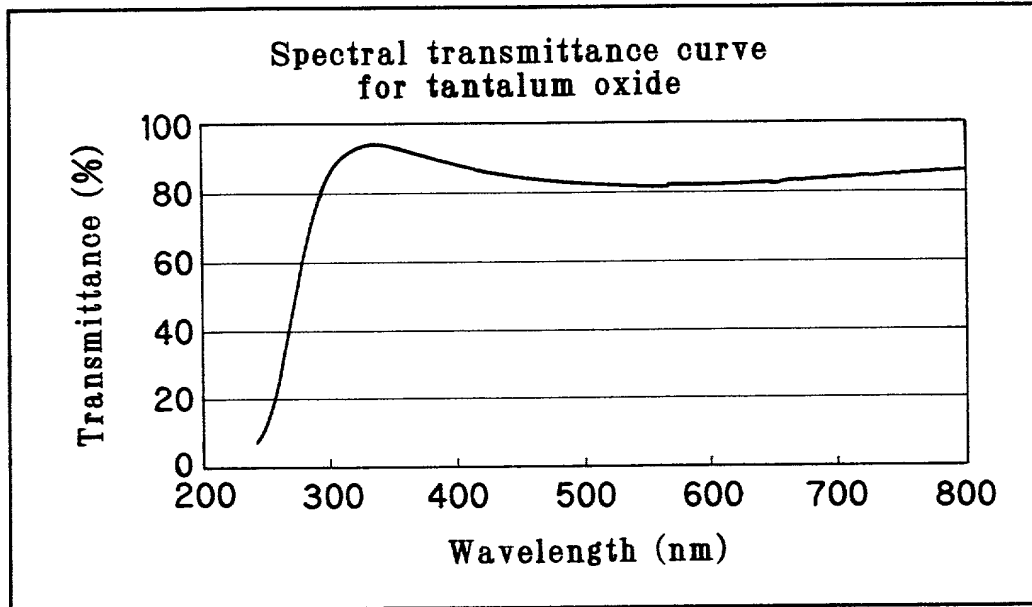
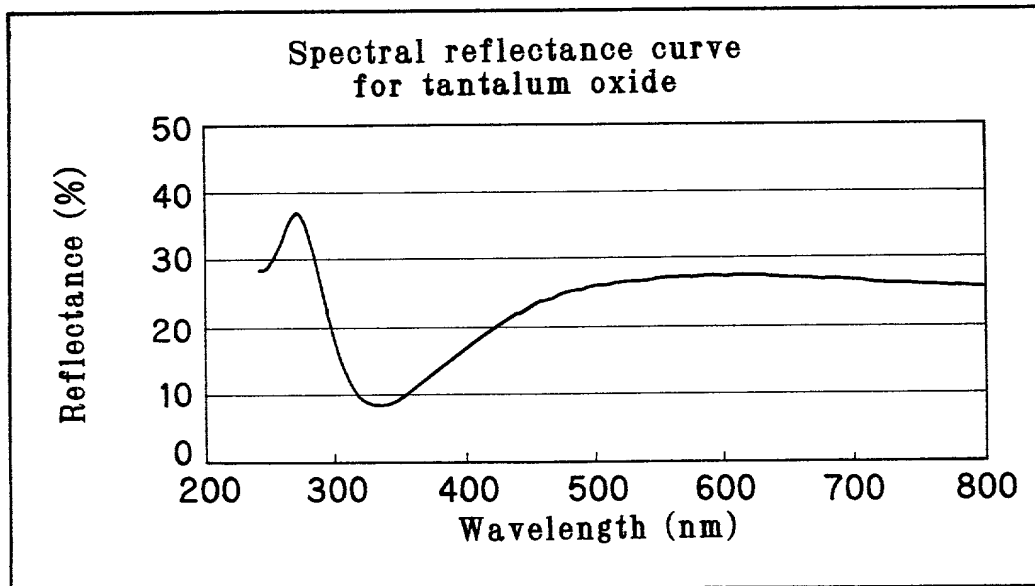


FIG. 12



DAJ9-800N-P

Attorney's Docket No. A-398

COMBINED DECLARATION AND POWER OF ATTORNEY
(ORIGINAL APPLICATION)

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name, I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

HALFTONE PHASE SHIFT PHOTOMASK, AND HALFTONE PHASE SHIFT PHOTOMASK BLANK FOR THE FABRICATION OF THE SAME

the specification of which is attached hereto unless box (a) or (b) is checked, in which case

(a) ☐ the specification was filed on _____ as Application Serial No. _____.

(b) ☒ the specification was filed as PCT International Application No. PCT/JP00/06038 filed on September 6, 2000 and was amended under PCT Art. 19 on _____ (if any).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, sec. 1.56.

I have identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America and filed less than 12 months (6 months for designs) prior to this United States application and of which I claim foreign priority benefits under Title 35, United States Code, sec. 119, and I have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

EARLIEST FOREIGN APPLICATION, AND ALL FOREIGN APPLICATIONS FILED MORE THAN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO THIS U. S. APPLICATION

<u>Country</u>	<u>Application No.</u>	<u>Date of Filing</u> (Month/day/year)
JAPAN	11-255746	09/09/99
_____	_____	_____
_____	_____	_____

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As a named inventor, I hereby appoint the following attorneys to prosecute this application and transact all business in the Patent and Trademark Office connected therewith and in connection with the resulting patent:

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I authorize the attorneys that I have appointed to accept instructions regarding this application and the resulting patent from Azusa Patent Office.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Title 18, United States Code, sec. 1001, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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